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Synthesis and Polymerization of 1-(2-N-Aziridinoethyl)-4-vinylbenzene

Kazunori Kataoka and Teiji Tsuruta*

Department of Synthetic Chemistry, Faculty of Engineering,
University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113, Japan

ABSTRACT

An addition reaction of aziridine onto 1,4-divinylbenzene(DVB) catalyzed by lithium aziridide was studied. It was found that 1-(2-N-aziridinoethyl)-4-vinylbenzene(AEVB) and 1,4-bis(2-N-aziridinoethyl)-benzene(BAEB) can be prepared selectively under appropriate conditions. On the basis of kinetic studies, the reactivity of aziridine toward DVB was compared with that of diethylamine. Vinyl polymerization and ring-opening polymerization of AEVB were also carried out to obtain poly[1-{4-(2-aziridinoethyl)phenyl}ethylene] (poly(AEPE)) and poly[{(4-vinylphenethyl)imino}-ethylene](poly(VPIE)), respectively.

INTRODUCTION

The importance of polymers possessing alkylamino substituents is being increased in the field of biomedical or environmental application.

In a previous paper, we reported the convenient synthesis of 1-(2-diethylaminoethyl)-4-vinylbenzene (EAVB) from 1,4-divinylbenzene(DVB) and diethylamine catalyzed by lithium diethylamide-diethylamine complex (TSURUTA et al, 1976). Polymers derived from EAVB exhibited a unique behavior as the biomedical material (KATAOKA and TSURUTA, 1978a: KATAOKA et al, 1978b).

By carrying out the addition reaction of DVB with a variety of acyclic and cyclic amines using lithium alkylamide as catalyst, a variety of functional monomers possessing alkylamino substituents can be synthesized. This paper is concerned with a study of synthesis of 1-(2-N-aziridinoethyl)-4-vinylbenzene(AEVB) by the addition reaction of aziridine with DVB. The polymerization behavior of AEVB is also reported. As AEVB

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has two types of functional group, i.e., vinyl group and aziridino group, the polymer derived from AEVB will be useful as a reactive polymer.

EXPERIMENTAL

Most of the experiments were carried out under a purified nitrogen atmosphere.

Reagents: All solvents used were purified by usual methods. Aziridine was distilled from calcium hydride. Butyllithium (BuLi) was prepared according to the literature and was used as a cyclohexane solution(GILMAN et al, 1940). 1,4-Divinylbenzene(DVB) was isolated from commercial DVB according to the method of STOREY(1965). Azobisisobutyronitrile(AIBN) was recrystallized from ethanol. 2,2'-Azobis-(2,4-dimethyl valeronitrile)(V-65) was supplied from Wako Pure Chemical Co. Methyl p-toluenesulfonate was purified by distillation.

Synthesis of 1-(2-N-aziridinoethyl)-4-vinylbenzene (AEVB): To the cyclohexane(10ml) solution of aziridine (11.4g, 0.26mole), 4.06ml of cyclohexane solution of BuLi(1.97M) was added. After a few minutes stirring, 31.3g(0.24mole) of DVB, dissolved in 13ml of cyclohexane, was injected via a syringe at 0°C. The mixture was stirred at 0°C for 25min. After stopping the reaction with methanol, the reaction mixture was washed with water followed by drying over $MgSO_4$. AEVB was isolated by a fractional distillation under reduced pressure, bp 76°C(0.18mmHg), yield 61%. The Carbon-13 NMR spectrum was in agreement with the assumed structure of AEVB(see FIG.2a).

$C_{12}H_{15}N$(173.3) Calc. C 83.19, H 8.73, N 8.08
Found C 82.54, H 8.82, N 7.83

A small amount of the second addition product, 1,4-bis(2-N-aziridinoethyl)benzene(BAEB), was also distilled as the final fraction, bp 122°C(0.17mmHg), yield 7%. The Carbon-13 NMR spectrum was in agreement with the assumed structure of BAEB.

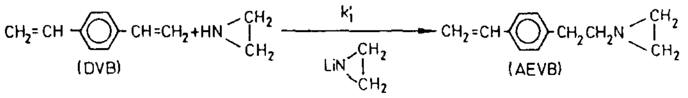
Procedure of rate study: The methods of the rate study of the addition reaction were described in a previous paper(NARITA et al, 1973).

Polymerization procedure: Polymerization was carried out in a sealed ampoule with stirring. After a definite period of time, the ampoule was opened and the contents were poured into a large excess of hexane at the dry ice-ethanol temperature. The precipitated polymer was re-dissolved into benzene and subjected to freeze-drying.

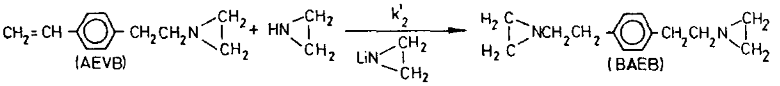
RESULTS and DISCUSSION

Selective preparation of AEVB and BAEB

The addition reaction of aziridine with DVB catalyzed by lithium aziridide is considered to proceed stepwise via the following equation:



(i)



(ii)

It was found that DVB was selectively converted to AEVB with a formation of negligible amount of BAEB under the condition described in the Exptl. Part. This means that the rate of the first addition reaction(k_1) is markedly larger than that of the second addition reaction(k_2) similarly to the reaction between DVB and diethylamine. By carring out this addition reaction under excess of aziridine with a longer reaction time, DVB was converted to BAEB almost quantitatively. MANECKE and HELLER(1962) reported that BAEB was synthesized from DVB(mixture of *meta* and *para* isomers) and aziridine catalyzed by metallic sodium. No data, however, were reported on the selectivity of sodium catalyst.

TABLE 1

Pseudo first-order rate constants k_1' of the reaction of lithium dialkylamide with DVB[a)].

$[\text{amine}]_0$	$[>\text{NLi}]_0$	solvent	temp.	k_1'
mol/l	mol/l		°C	hr^{-1}
aziridine(0.25)	0.025	THF	30	38.4
aziridine(0.20)	0.020	THF	30	32.2
aziridine(0.125)	0.0125	THF	30	21.6
aziridine(1.0)	0.1	cyclohexane	50	15.3
diethylamine(1.0)	0.1	cyclohexane	50	3.5[b)]

a) $[\text{DVB}]_0 = 0.125$ mol/l

b) Taken from the work cited in reference(TSURUTA et al, 1976).

Kinetic studies of the addition reactions

The addition reaction of aziridine onto DVB was found to be a first-order reaction with respect to [DVB] similarly to that of diethylamine(TSURUTA et al, 1976). The reaction rate v_1 is expressed as in Eq.(iii).

$$v_1=k_1'[\mathrm{DVB}] \qquad \text{(iii)}$$

where

$$k_1'=k_1[\mathrm{LiN}\!<]^x \qquad \text{(iv)}$$

The pseudo first-order rate constants are summarized in TABLE 1.

As shown in FIG.1, the slope of the straight line obtained from the plot of log k_1' vs log$[\mathrm{LiN}\!<]$ was found to be 0.94 when THF was used as solvent. Therefore, the reaction rate can be expressed as Eq.(v), and k_1 is calculated as (0.45±0.02)l/mol·sec(30°C).

$$v_1=k_1[\mathrm{DVB}][\mathrm{LiN}\!<] \qquad \text{(v)}$$

In cyclohexane, however, the reaction system became heterogeneous when the concentration of aziridine was below 0.5M. This system was not adequate to the rate analysis. The reason of heterogeneity may be due to the poor solubility of lithium aziridide to cyclohexane.

It is to be noted that the reactivity of aziridine toward DVB is remarkably higher than that of diethylamine. The higher reactivity of aziridine should be explained by the less steric requirement compared with diethylamine.

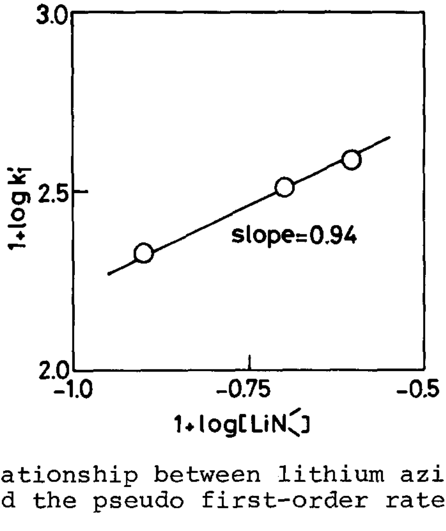


FIG.1 Relationship between lithium aziridide concentration and the pseudo first-order rate constant k_1'

TABLE 2

Results of Polymerization of AEVB

[AEVB] mol/l	solvent	initiator		temp. °C	time hr	yield[c] %
		type	mole ratio to AEVB			
1.3	Benzene	AIBN	1/250	60	17	35.6[d]
1.3	Benzene	AIBN	1/100	60	8.5	19.9[e]
1.3	Benzene	V-65[a]	1/100	60	5.5	32.0[f]
1.3	Benzene	V-65	1/100	45	13	30.8[e]
0.6	Acetonitrile	MT[b]	1/17	25-45	120	24.7[g]
0.5	Acetonitrile	MT	1/72	40	43	7.2[f]
0.6	Acetone	MT	1/20	25	120	26.0[g]

a) V-65 = 2,2'-Azobis-(2,4-dimethyl valeronitrile)
b) MT = Methyl p-toluenesulfonate
c) Hexane insoluble fraction at -50°C
d) Gel, e) Powder, f) Gum, g) Grease

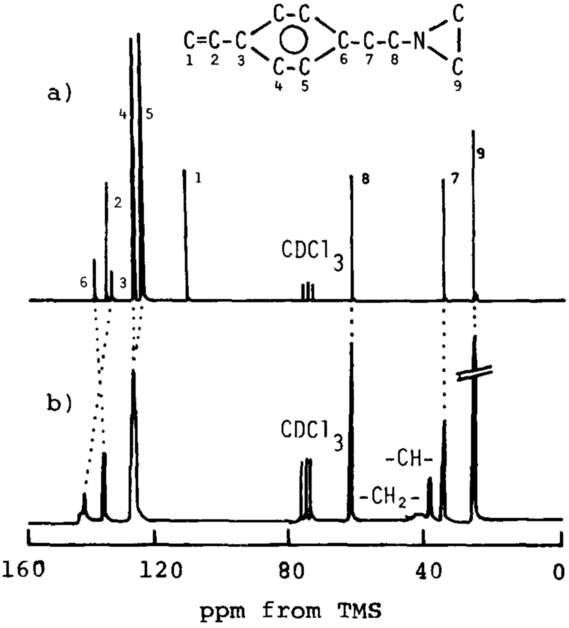


FIG.2 Carbon-13 NMR spectra of a) AEVB, and b) poly(AEPE) obtained by radical polymerization.

Polymerization of AEVB

The results of the polymerization of AEVB are summarized in TABLE 2.

The radical polymerization of AEVB was carried out by using AIBN as initiator at 60°C. Gellation was observed to take place before the conversion of AEVB reached 30%.

When the polymerization was carried out with V-65 as initiator at 45°C, a soluble polymer was able to be isolated as white powder even though the conversion of AEVB went up over ca. 30%. As shown in FIG.2b, the polymer obtained maintains aziridine ring intact on the side chain, and was identified as poly[1-{4-(2-aziridinoethyl)phenyl}ethylene](poly(AEPE)).

Poly(AEPE) thus obtained gradually became insoluble on standing, and rapidly formed gel by mixing it with alkyl halides such as allyl bromide.

The ring-opening polymerization of AEVB was also carried out by using methyl p-toluenesulfonate as initiator, which is known to be inactive toward vinylbenzene. The polymer obtained was soluble in chloroform and THF. The IR and NMR spectra showed that the groups involved in this polymerization were primarily the aziridino groups but not the vinyl groups. The polymer obtained was concluded to have a structure of poly[{(4-vinylphenethyl)imino}ethylene](poly(VPIE)). From GPC measurements, poly(VPIE) thus obtained seemed to be in the region of oligomer.

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